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Effect of Sugar on Mortars.

INTERESTING results have been obtained from a recent research in Spain by J. Basso, chief chemist of the Asland Cement Co., in order to ascertain the effect of the addition of sugar and honey to white lime and Portland cement mortars.

Quick lime, prepared by burning a pure Triassic limestone, was slaked with 55 per cent. of water and the calcium hydrate thus obtained was sieved through a No. 76 sieve (900 meshes to the square centimetre). The sand added to the lime was plain standard sand (Leucate sand). Additions of sugar and honey were made, at the rate of 6 per cent. of each of these substances to the mixing water, and the test pieces were hand made without ramming. The results are given in Table I.

TABLE I.

	Age (days).	Tensile strength (lb. per square inch).	Compressive strength (lb. per square inch).
Lime mortar without sugar	7	Nil	Nil
	28	52.5	122
Lime mortar with 6 per cent. of sugar ..	7	64	56.8
	28	88	180
Lime mortar with 6 per cent. of honey ..	7	39.8	Nil
	28	78	130.5

In order to ascertain the influence on these strengths of carbonation of the lime, the quantity of carbon dioxide fixed by the test pieces was determined in each case. This was found to be almost twice as great in the mortars without sugar as in those containing sugar. The increase of strength produced by sugar, probably due to the formation of calcium saccharate, is apparent. Hardening by saccharose is mainly produced on the surface, inasmuch as the test pieces

(259)

made with the addition of sugar have such a hard crust at 28 days that it cannot be scratched with a copper coin, whilst the test pieces with no sugar are easily scratched. This coat increases with age, and progresses towards the middle of the test piece.

In the experiments on the addition of sugar to Portland cement a standard cement was used with an initial set of three hours ten minutes and a final set of six hours ten minutes. Both neat cement and 1 : 3 sand-cement mortar test pieces were prepared. The results are shown in Table II.

TABLE II.

Mortar.	Age (days).	Tensile strength (lb. per square inch).	Compressive strength (lb. per square inch).
Neat cement	1	405	—
	7	805	9,380
	28	783	11,950
1 : 3 cement and sand	1	336	2,550
	7	400	4,970
	28	443	5,810

Additions of 6 per cent. of sugar (by weight) to the neat cement paste, and of 2.5 per cent. (by weight of the cement) to the 1 : 3 cement-sand mortar, were then tested. The test pieces were so badly disintegrated after a few days' storage that it was impossible to make any strength tests. The specimens were quick setting, with an initial set of twelve minutes and a final set of fifteen minutes only.

The addition to such a cement of one-half of 1 per cent. of sugar reduced its initial set to one-half, and the final set to two-thirds, of the ordinary time. The tensile strengths of the neat pastes were considerably lowered at twenty-four hours (from 394 to 67 lb. per square inch), and very slightly reduced at twenty-eight days (from 768 to 760 lb. per square inch). On the other hand, the compressive strength at seven days increased from 7,400 to 9,000 lb. per square inch, and remained constant at twenty-eight days at 10,500 lb. per square inch.

For the 1 : 3 mortar the tensile strengths showed the following changes : At twenty-four hours, from 244 to 64 lb. per square inch ; at three days, from 258 to nil lb. per square inch ; at five days, from 284 to 71 lb. per square inch ; at seven days, from 291 to 255 lb. per square inch ; at twenty-eight days, from 380 to 450 lb. per square inch. The compressive strengths underwent the following alterations : At twenty-four hours, from 1,560 to nil lb. per square inch ; at three days, from 2,410 to 569 lb. per square inch ; at five days, from 3,120 to 1,840 lb. per square inch ; at seven days, from 3,690 to 3,840 lb. per square inch ; at twenty-eight days, from 5,250 to 5,970 lb. per square inch.

The latter tests, with the addition of 0.5 per cent. of sugar, show a remarkable delay in the initial hardening, although the later strengths are normal. The following explanation is suggested. When mixing Portland cements their aluminate, silicate, and ferrite compounds are attacked by water, with the liberation of calcium hydrate, until a supersaturated calcium hydrate solution is formed. When the setting and hardening processes take place the first components entering into reaction are the aluminates; later and more slowly the silicates and ferrites. In usual practice the presence of calcium hydrate in saturated solution is necessary in order that these reactions may take place. If for any reason this solution is not formed the reaction of the aluminates is hastened and quick setting takes place.

When setting and hardening processes develop in the presence of a sugar solution they cannot do so normally, as the calcium hydrate liberated enters into combination with saccharose to produce calcium saccharate. The formation of this compound absorbs all the calcium hydrate that should have remained in solution for the setting process; in this manner it hastens the reaction of the aluminates and produces the quick set as noticed in the cement to which 6 per cent. of sugar was added. On the other hand, on account of the quick set and of the loss of mixing water ensuing from the rise of temperature (about 18 deg. F.) in the mass, the silicates react very slightly and normal hardening cannot take place. The calcium saccharate formed causes an increase of volume and gives rise to unsoundness in the test pieces.

By reducing the percentage of sugar, although some calcium saccharate is also formed there is still enough free calcium hydrate available and setting can take place, although it does so more slowly and with less increase of temperature. The reaction of the silicates becomes normal, but occurs later.

The results of the research show that sugar has a favourable effect on white lime mortars and an injurious effect on Portland cement mortars, but in any case the advantages implied by the addition of sugar in the first instance are not balanced by the cost of sugar, however low its price may be, as a very poor Portland cement mortar (1 : 5 or 1 : 6) gives far better strengths at still lower prices.

The Japanese Cement Industry.

According to a report on " The Economic Conditions in Japan," prepared by officials at the British Embassy in Tokyo and issued by H.M. Stationery Office (price 3s. 6d. net), the paid-up capital of the twelve companies forming the Japanese Portland Cement Association is about 132 million yen. There are in all fifteen companies, controlling thirty-five factories, whose total output in December 1932 was 370,000 metric tons. Wholesale quotations in January 1933 were yen 4.20 per barrel or yen 24.30 per metric ton. The cost of production is estimated at yen 2.80, equivalent at current exchange rate to 3s. 6d. per barrel. Exports of cement from Japan were valued at 10,066,000 yen in 1930, 9,089,000 yen in 1931, and 8,545,000 yen in 1932. The principal exports were to Dutch East Indies (2,600,000 yen in 1932), Hongkong (2,047,000 yen) and British India (1,307,000 yen).

Heat Transmission in Rotary Kilns.—IV.

By W. GILBERT, Wh.Sc., M.Inst.C.E.

(74) It is now proposed to work out in detail the heat transmission in the 202 ft. kiln which was referred to in Part I of this series of articles (CEMENT AND CEMENT MANUFACTURE, December, 1932). This is a simple case, but the method is applicable to longer kilns containing chains or slurry lifters, as will be seen later.

Various details relating to a test on this kiln, together with a heat balance, were given in CEMENT AND CEMENT MANUFACTURE for November, 1930, but one or two modifications are now made.

(a) The kiln exit-gas temperature was measured at 884 deg. F. by a pyrometer not protected against radiation loss ; the correct value is now estimated to be 950 deg. F.

(b) The heat balance included for exothermic reaction and excess heat unaccounted for a quantity of standard coal equal in weight to 2.34 per cent. of the clinker produced, this item being obtained by difference. Since a standard value of 1.35 per cent. is now used for the exothermic reaction, the apparent coal consumption of this particular kiln has to be increased and the heat required to decompose the $CaCO_3$ somewhat diminished in order to maintain a balance between the coal burned and the heat accounted for.

The figures as revised are, however, representative of the performance of a kiln of this size operating without chains or slurry lifters.

(75) Various particulars relating to the test which will be required for calculation purposes are as follows :—

    (a) Clinker output per minute   260 lb.
    (b) Dry coal, as fired, per minute   77.40 ,,
    (c) Air per minute   1,058 ,,
    (d) Dry coal as fired per 100 lb. of clinker ..   29.75 ,,
    (e) Standard coal per 100 lb. of clinker   31.90 ,,
    (f) CO_2 from raw material per 100 lb. of clinker ..   50.90 ,,
    (g) Steam from slurry per 100 lb. of clinker   121.50 ,,

(76) In the calculations which follow heat quantities are expressed in two ways : (x) as lb. of standard coal per 100 lb. of clinker, or more simply as percentages ; (y) as B.T.U.'s per pound of dry coal as fired.

In this kiln a heat expenditure of 1 lb. of standard coal (or 12,600 B.T.U.'s) per 100 lb. of clinker is equivalent to $\dfrac{12,600}{29.75}$ or 423.7 B.T.U.'s per pound of dry coal as fired. Hence we can pass from (y) to (x) on dividing by 423.7.

Heat Content of Gases.

(77) It will frequently be necessary to refer to the heat content per pound of the gases CO_2, H_2O, N_2, and air at various temperatures, and for this purpose

Table VII has been prepared.   The specific heats used are from the text book by Partington and Shilling.   To obtain the total heat of the steam above 60 deg. F. in col. (5) it is necessary to add $152 + 970 = 1,122$.

The heat content at intermediate temperatures can be obtained by interpolation, but a graph based on the table and plotted on paper ruled in millimetres will be found very useful.

TABLE VII.

HEAT CONTENT OF GASES IN B.T.U.'S PER POUND.

(1). Gas temperature deg. Fah.	Heat above 60 deg. F.			(5). H_2O above 212 deg. F.
	(2). CO_2.	(3). N_2.	(4). Air.	
60	—	—	—	—
212	31.0	37.8	36.6	—
392	69.3	82.8	80.1	87.7
572	109.2	127.9	123.7	174.1
752	150.7	173.3	167.5	260.4
932	194.1	218.9	211.6	347.4
1,112	238.0	264.8	256.0	435.2
1,292	283.8	311.0	300.6	524.9
1,472	330.8	357.8	345.7	616.6
1,652	379.0	405.0	391.3	710.7
1,832	428.2	452.4	437.2	809.0
2,012	478.5	500.5	483.7	909.0
2,192	529.6	549.2	530.7	1013.0
2,372	581.7	598.4	576.4	1123.0
2,552	634.5	648.2	626.3	1236.0
2,732	688.0	698.5	675.0	1355.0

The Products of Combustion.

(78) The heat content of each of the gaseous products of combustion at the flame temperature of 2,450 deg. F. is now calculated; the result is shown in Table VIII.

TABLE VIII.

(PRODUCTS OF COMBUSTION AT 2,450 DEG. F.).

	CO_2.	H_2O.	N_2.	Excess Air.	Total.
					lb.
Weight of gas per lb. of dry coal as fired (lb.)	2.89	0.43	8.11	3.12	14.55
Heat per lb. of gas above 60 deg. F. (B.T.U.)	605	2,294	620	598	—
Heat of gas per lb. of dry coal as fired (B.T.U.)	1,748	985	5,020	1,865	B.T.U.'s 9,618

By para. (76) the total heat of the products of combustion at flame temperature is also

$$\frac{9,618}{423.7} = 22.71 \text{ per cent.}$$

(79) It will be necessary later to ascertain the heat content of the products of combustion, the CO_2 from the raw material, and the steam from the slurry at various temperatures between 950 deg. F. and 2,450 deg. F. The calculations are made by the aid of Table VII, and the result is shown in Table IX. The figures in the first line are obtained by the method described in para. (78). In the second line the weight of the CO_2 is taken from para. (75f), and the heat content per pound from Table VII. At 950 deg. F., for instance, the result is

$$\frac{50.9 \times 200}{12,600} = 0.81 \text{ lb. standard coal.}$$

The total heat of the slurry steam at various temperatures can be obtained in a similar manner.

Rearrangement of the Kiln Heat Balance.

(80) The quantities which make up the heat balance are now rearranged in order to show in proper order the heat which has to be transmitted in the various stages as the material travels down the kiln.

The calculations are based on 100 lb. of clinker.

	Standard coal, lb.	
(a) EVAPORATION OF SLURRY MOISTURE.—		
100 lb. of raw material raised from 60 deg. to 212 deg. F. ($\phi = 0.25$)	0.30	
50.9 lb. of CO_2 (incorporated) raised from 60 deg. to 212 deg. F. ($\phi = 0.21$)	0.13	
121.5 lb. of water raised from 60 deg. to 212 deg. F.	1.46	
121.5 lb. of water evaporated from and at 212 deg. F. (L = 970)	9.35	
121.5 lb. of steam superheated to 950 deg. F. ($\phi = 0.484$)	3.43	
Radiation from kiln shell	0.76	
		15.43
(b) RAISING RAW MATERIAL TEMPERATURE.—		
100 lb. of raw material raised from 212 deg. to 1,300 deg. F. ($\phi = 0.25$)	2.16	
50.9 lb. of CO_2 incorporated raised 212 deg. to 1,300 deg. F. ($\phi = 0.234$)	1.03	
Radiation from kiln shell	0.21	
		3.40
(c) DECOMPOSITION OF $CaCO_3$.—		
100 lb. of raw material raised 1,300 deg. to 1,700 deg. F. ($\phi = 0.25$)	0.79	
50.9 lb. of CO_2 (incorporated) raised 1,300 deg. to 1,500 deg. F. ($\phi = 0.257$)	0.21	
Decomposition of 116 lb. of $CaCO_3$	6.57	
Radiation from kiln shell	0.51	
		8.08
(d) RAISING MATERIAL TEMPERATURE AND CLINKERING.—		
100 lb. material raised from 1,700 deg. to 1,850 deg. ($\phi = 0.255$)	0.30	
100 lb. material raised from 1,850 deg. to 2,450 deg. by the exothermic reaction ($\phi = 0.284$)	1.35	
Radiation from kiln shell	0.12	
		1.77
(e) THE KILN DEAD END.—		
Heat received by flame radiation	0.36	0.36
Total	—	29.04

(81) In this statement the symbol ϕ denotes the mean specific heat over the temperature range considered. To illustrate the method of calculation take, for instance, the first item in para. (80b), which is 100 lb. of raw material raised from 212 deg. to 1,300 deg. F. Since the temperature range is 1,088 deg. F. the heat required expressed in lb. of standard coal will be

$$\frac{100 \times 1,088 \times 0.25}{12,600} = 2.16$$

The shell radiation in each section is found by multiplying the heat given to the material by 0.068 (refer to Part III, para. (53) of this series, June, 1933).

The CO_2 from the raw material is decomposed at an average temperature of 1,500 deg. F. It mixes with the products of combustion and the combined gases are assumed to reach a common temperature of 2,450 deg. F. when combustion is complete. The heat required to raise the CO_2 from 1,500 deg. to 2,450 deg. F. is, by Table IX, $2.46 - 1.37 = 1.09$ lb. of standard coal per 100 lb. of clinker.

TABLE IX.

TOTAL HEAT, ABOVE 60 DEG. F., OF THE KILN GASES AT VARIOUS TEMPERATURES
EXPRESSED IN LB. OF STANDARD COAL PER 100 LB. OF CLINKER.

Description.	Gas Temperatures in Degrees Fah.					
	950.	1,200.	1,500.	1,800.	2,100.	2,450.
Products of combustion	8.70	10.95	13.67	16.47	19.32	22.71
CO_2 from raw material	0.81	1.06	1.37	1.70	2.05	2.46
Steam from slurry..	14.24	15.43	16.89	18.43	20.05	—

Details of the Heat Supply.

(82) The clinker finally attains a temperature of 2,450 deg. F., and its total heat per 100 lb. above 60 deg. F., taking $\phi = 0.258$, is

$$\frac{(2450 - 60) \times 100 \times 0.258}{12,600} = 4.90 \text{ lb. standard coal.}$$

From the kiln heat balance previously given the cooler radiation and the hot clinker loss at the cooler delivery end amounted to 0.83 per cent. There is also a heat loss in the kiln dead end of 0.14 per cent., to be explained later, hence the heat content of the air supplied to the combustion zone is $4.90 - 0.83 - 0.14 = 3.93$ per cent.

The total heat supply to the combustion zone of the kiln is therefore

	Per cent.
(a) From the coal as fired, by para. (75, e)	31.90
(b) By air pre-heated	3.93
Total	35.83
The heat supplied to the kiln gases is :—	
(c) To the products of combustion, see para. (78) 22.71	
(d) To the CO_2 from the raw material, see end of para. (81) 1.09	23.80
Hence the heat radiated from the burning coke particles is by difference	12.03

(83) We can now set down in detail the sources from which heat is supplied to the material inside the kiln.   They are as follows :—

	Per cent.
(a) By radiation from the coke particles..	12.03
(b) By the exothermic reaction (standard value)	1.35
(c) By the heat liberated from the products of combustion and the CO_2 from the raw material falling from 2,450 deg. to 950 deg. (see Table IX), 22.71 — 8.70 + 2.46 — 0.81	15.66
Total	29.04

This compares with the total in para. (80).

Heat Transmitted by Gas Radiation and Convection.

(84) It is now proposed to deal with that portion of the kiln in which the heat is transmitted by gas radiation and convection.   The total quantity available is, by para. (83c), 15.66 lb. of standard coal per 100 lb. of clinker, or 15.66 per cent. For calculation purposes this portion of the kiln is divided into six stages.   In stage (1) the slurry is raised in temperature from 60 deg. to 212 deg. F., and in each of the stages 2, 3, 4 and 5 one-fourth of the slurry moisture is evaporated. The heat so far expended is 15.43 per cent., see para. (80, a). The remainder of the heat, i.e., 0.23 per cent., is sufficient to raise the temperature of the dry raw material, and the CO_2 incorporated from 212 deg. to 285 deg. F. ; this constitutes stage (6).

To calculate the gas temperature at the end of each stage, the heat which it must contain, reckoned above 950 deg. F., is set down in Table X, the figures being taken from para. (80).

TABLE X.

	Heat per cent. Required in the Gas at the end of each Stage.					
	(1).	(2).	(3).	(4).	(5).	(6).
Raising slurry temperature ..	1.89	1.89	1.89	1.89	1.89	1.89
Evaporation of moisture	—	2.33	4.67	7.01	9.35	9.35
Superheat to 950 deg. F.	—	0.86	1.72	2.58	3.43	3.43
Raising temperature of dry material	—	—	—	—	—	0.22
Shell radiation loss	0.13	0.28	0.44	0.60	0.76	0.77
Total	2.02	5.36	8.72	12.08	15.43	15.66

(85) From the data given in Table IX a graph is drawn (see Fig. 16) which gives the total heat of the products of combustion, the CO_2 from the raw material, and the steam, reckoned above the exit gas temperature of 950 deg. F.   The heat due to one, two and three-fourths of the slurry steam is also shown.

At the end of stage (1) or at the beginning of stage (2) the kiln gases consist of the products of combustion, the CO_2, and all the slurry steam, and the available
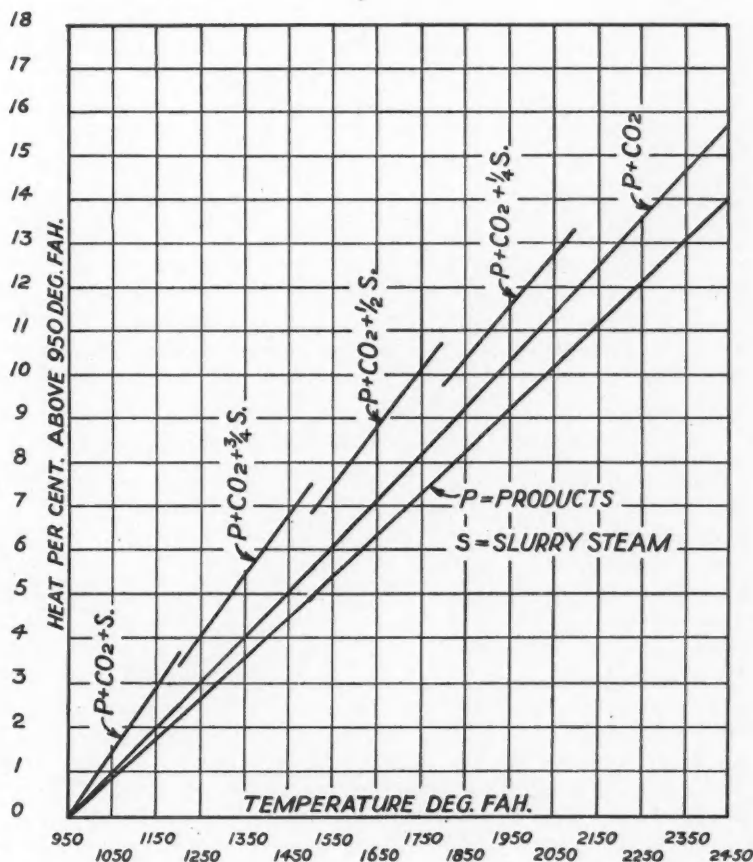
Fig. 16.

heat above 950 deg. F., by Table X, must be 2.02 per cent.; hence from the " all steam " line of the graph the required gas temperature is 1,085 deg. F.

At the end of stage (2) the gas consists of the products, the CO_2, and three-fourths of the slurry steam. Its available heat, from Table X, must be 5.36 per cent.; hence from the ¾ steam line on the graph, the gas temperature is 1,346 deg. F.

Proceeding in this manner the gas temperatures at the end of the remaining stages are calculated, the results being given in Table XI. To give perspective, the kiln length found necessary for each stage is also shown.

TABLE XI.

Position.				Material Temperature, Deg. F.	Gas Temperature, Deg. F.	Length Required for Stage, Ft.
At beginning of stage ..		..	(1)	60	950	—
At end of stage..	..	..	(1)	212	1,085	40.2
,,	,, ..	.. ..	(2)	212	1,346	37.0
,,	,, ..	.. ..	(3)	212	1,646	25.7
,,	,, ..	.. ..	(4)	212	2,000	18.5
,,	,, ..	.. ..	(5)	212	2,427	16.0
,,	,, ..	.. ..	(6)	285	2,450	1.6

It will be noticed that the average temperature of the material is assumed to remain at 212 deg. F. until all the moisture is expelled. This point was referred to in para. (13) of Part I of this series. The experiments are being continued and will be described later, but it is apparent that the error due to this assumption is small.

Convection Constants and P.D. Values.

(86) Owing to the evolution of steam from the slurry and to the varying gas temperature, the weight of gas flowing per hour and the gas velocity will vary in each stage. It is necessary to examine the subject in some detail in order to obtain data for the calculation of heat transmission. The essential figures are gathered together in Table XII, a description of which is as follows :

LINES 1 TO 5.—From the data given in para. (75) it will be seen that there are 4.08 lb. of slurry steam and 1.72 lb. of CO_2 from the raw material per pound of dry coal as fired. The weights of the products of combustion per pound of dry coal are given in Table VIII. The added values occur in stage (1). The weights in the remaining stages only differ in respect of the quantity of moisture which has been evaporated from the slurry. Unlike Table XI the figures of Table XII relate to the average values for each stage.

LINES 6 TO 8 are obtained from the gas weights by remembering that the volumes of the various gases in cubic feet per pound at 32 deg. F. are CO_2, 8.15 ; H_2O, 19.91 ; N_2 12.76 ; and air, 12.38. The appropriate volumes for N_2 and air are included in line 8.

LINE 11.—From para. (75, b) the dry coal fired per hour is 60 × 77.4 lb., hence using lines 5 and 10 the value of W is obtained for each stage. This value is often used to calculate the rate of heat transfer by convection, and for this reason it has been listed.

LINE 12.—This is obtained from Table XI.

LINE 13.—This can be obtained from lines 8 and 12, since the gas volume is proportional to the absolute temperature.

LINE 14.—The dry coal per second is 1.29 lb. and the result follows from lines 10 and 13.

TABLE XII.

PRELIMINARY DATA FOR STAGES (1) TO (6).

(The figures given are average values for each stage.)

Line No.			Stage Numbers.					
			(1).	(2).	(3).	(4).	(5).	(6).
1	Average weight of kiln gases per pound of dry coal	CO_2	4.61	4.61	4.61	4.61	4.61	4.61
2		H_2O	4.51	4.00	2.98	1.96	0.94	0.43
3		N_2	8.11	8.11	8.11	8.11	8.11	8.11
4		Air	3.12	3.12	3.12	3.12	3.12	3.12
5		lbs.	20.35	19.84	18.82	17.80	16.78	16.27
6	Volume of kiln gases per pound of dry coal (In cubic feet, at 32° F.)	CO_2	37.6	37.6	37.6	37.6	37.6	37.6
7		H_2O	90.0	79.6	59.4	39.0	18.7	8.6
8		Total	269.8	259.4	239.2	218.8	198.5	188.4
9	Kiln diameter inside lining, feet..		7.65	7.65	7.65	7.65	7.65	7.65
10	Area of cross section in square feet		46.0	46.0	46.0	46.0	46.0	46.0
11	Gas per hour per square foot of cross section = W lb.		2,055	2,000	1,900	1,798	1,692	1,641
12	Average gas temperature in stage deg. F. ..		1,017	1,215	1,496	1,823	2,213	2,438
13	Volume of kiln gases per lb. of dry coal at average stage temperature, cu. ft. ..		808	880	945	1,010	1,077	1,110
14	Gas velocity in feet per second ..		22.6	24.7	26.5	28.3	30.2	31.1
15	Convection } (a) gas and material		1.91	1.89	1.87	1.85	1.82	1.78
16	Constant Hc } (b) gas and lining ..		1.88	1.83	1.76	1.65	1.55	1.50
17	Values } (a) for H_2O ..		2.56	2.35	1.90	1.36	0.72	0.35
18	of PD } (b) for CO_2 ..		1.07	1.11	1.20	1.31	1.45	1.53

LINES 15 AND 16.—The average material temperature in each stage can be obtained from Table XI, and the average lining temperature from Table XIII which will follow. The calculation is then made by the aid of Table VI in Part II of this series. The lining temperature is not known in the first instance, but it can be approximately estimated and adjustment made later.

LINES 17 AND 18.—The fraction of each gas present by volume is denoted by P and is obtained from lines 6 to 8, and D, the kiln diameter in feet, is given in line 9. For example the value of PD for the H_2O in stage 1 is

$$\frac{90.0}{269.8} \times 7.65 = 2.56.$$

The values of P.D. are required in order to calculate the heat transmitted by gas radiation in each stage. The data necessary for the calculation of the stage lengths in the gas radiation and convection zone are now complete.

Trade Notice.

EXCAVATORS.—Messrs. Ruston-Bucyrus, Ltd., have issued a new and well-illustrated catalogue describing their " No. 4 Universal " ½-yd. excavator, in which several improvements have recently been made. Copies will be sent on application to the Company's offices at Lincoln.

Government Control of Cement Manufacture in Ireland.

THE Cement (No. 2) Bill, 1933, giving the Government of the Irish Free State power to control the manufacture and importation of cement has been passed by both Houses of the Parliament of that country, and it is anticipated that the Minister for Industry and Commerce will shortly announce when he proposes to put the Act into force.

Under the Act it is unlawful to manufacture cement in the Irish Free State without a licence issued by the Department of Industry and Commerce. These licences will specify the area in which the manufacturer may operate his factory, the extent to which the materials and plant used must be of Irish manufacture, the time at which manufacture must be commenced, the extent to which the capital invested in the business is owned by Irish Free State nationals (*i.e.*, persons born in the twenty-six counties of the Irish Free State, or who have resided there for five consecutive years before the application for the licence was made), the management of the business by Irish nationals, and the rate of wages to be paid.

The maximum and minimum quantities of cement to be produced by any one licensee during a year are controlled by the terms of the licences, and the standard of the product will be determined by the Minister for Industry and Commerce who will also make regulations governing the price, method of manufacture, and packing. Licences may be revoked at any time by order of the Minister.

Where the Government is satisfied that a person holding a cement manufacture licence is unable to acquire by agreement any land necessary for the purpose of his business the Minister may make a compulsory acquisition order after holding a local inquiry.

For the contravention of any of the terms of the licences heavy fines are to be imposed on summary conviction.

Importation of cement, which will be prohibited save under special licence, will be very restricted, and if in the opinion of the Minister the existing stocks of cement in the Irish Free State do not warrant the importation of further quantities, the application for an import licence will be refused. Licence fees will be calculated on a tonnage basis and will be payable before importation.

The Act also provides that inspectors of the Department of Industry and Commerce have power to inspect cement works and take samples of the product.

The late Mr. John Rolland.

We regret to announce the death, which took place on July 27, of Mr. John Rolland, who was in business as an engineer at Abbey House, Westminster, S.W.1. In his capacity as the English representative of Fried. Krupp A.G. and the Lurgigesellschaft für Waermetechnik (a branch of the Metallgesellschaft), Mr. Rolland was widely known in the cement industry.

The Hardening and Corrosion of Cement.—VI.

By Dr. KARL E. DORSCH

(Of the Technical High School, Karlsruhe, Baden)

The Influence upon Corrosion of Type of Cement and Nature of the Attacking Solution.

In the investigation of the behaviour of various cements in the presence of salt solutions, pure cements were used in the first series of experiments so as to eliminate the effect of such factors as the grading of the added materials. For the tests, 3-cm. cubes of cement were used, since it had previously been found that such small cubes were extremely suitable for the chemical study of the effect of aggressive solutions on different cements. The method has a number of advantages : we are working with chemically defined substances and the chemical transformations in the cement and the solution can be followed quantitatively; errors due to the unequal mixing of the mortar in the standard tests are avoided ; crystalline efflorescence formed on the cement can be submitted to more accurate microscopical examination than is the case with standard test-pieces ; thin
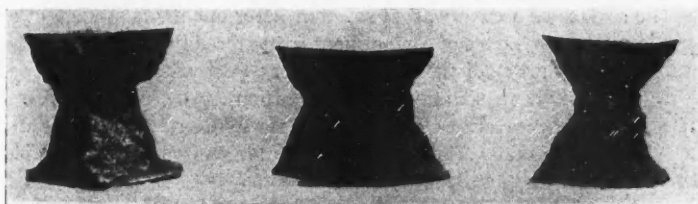
Fig. 44.—3-cm. cement cubes after crushing.

sections can be cut which give an accurate picture of the nature of the chemical attack ; and finally the crushing strength of small cubes presents more reliable results than tensile tests. Fig. 44 shows three of these 3-cm. cubes full-size after crushing.

TABLE VI.

	Ordinary Portland Cement.	High-strength Portland Cement.	Iron-ore Cement.	Blast-furnace Cement.	Portland-Jura Cement.	Aluminous Cement.
Insoluble residue ..	0.82	0.45	—	—	21.20	0.23
Loss on ignition ..	1.96	1.17	1.35	1.98	3.46	1.20
SiO$_2$	21.22	20.90	20.95	27.86	15.20	7.15
Al$_2$O$_3$	6.57	6.38	1.57	13.87	11.85	38.98
Fe$_2$O$_3$	2.89	3.12	7.94	0.86	2.32	5.75
FeO	—	—	—	1.05	1.08	3.26
CaO	63.55	65.44	65.35	48.94	41.75	42.00
MgO	1.60	1.46	0.70	2.28	1.17	0.25
SO$_3$	1.72	1.75	1.73	1.79	2.05	0.15
TiO$_2$	—	—	—	—	—	1.16
MnO	—	—	—	1.47	—	—

The investigation comprised six different cements, the types and percentage chemical analyses of which are given in Table VI.

The experiments upon cubes of pure cement will first be described. The conditions under which these cubes were prepared are summarised in Table VII.

TABLE VII.

	Percentage weight of Water.	Temperature of Water in Deg. C.	Temperature of Testing Room, Deg. C.	Humidity of Testing Room.	Initial Water Storage, Days.	Temperature of Attacking Solution, Deg. C.
Ordinary Portland cement	27	18	18	50	6	18
High-strength Portland cement ..	27	18	18	50	6	18
Iron-ore cement ..	27	18	18	60	6	18
Blastfurnace cement	29	18	18	60	6	18
Aluminous cement..	25	18	18	50	6	18

The average weights of the cubes, corresponding to the various specific gravities, were ordinary Portland cement 50 g., high-strength Portland cement 53 g., iron-ore cement 59 g., blastfurnace cement 51 g., and aluminous cement 58 g. The surface of a cube was 54 sq. cm. After one day's storage in air and six days in water, two cubes of each cement were stored in 500 c.c. of each of the following solutions : (1) distilled water, (2) 15 per cent. ammonium sulphate solution, (3) 15 per cent. sodium sulphate solution, (4) 15 per cent. magnesium sulphate solution, (5) saturated calcium sulphate solution, (6) 15 per cent. magnesium chloride solution. The solutions were not renewed and the cubes were examined daily.

The cubes stored in distilled water and saturated calcium sulphate solution showed no sign of attack after storage for eighteen months. Only in the case of the high-strength Portland cubes stored in calcium sulphate solution could hair cracks due to expansion be detected under the stereoscopic microscope. In the case of the cubes stored in ammonium, sodium, and magnesium sulphate solutions decomposition began after various periods shown in Table VIII.

TABLE VIII.

Solution.	Number of Days to Commencement of Attack.				
	High-strength Portland Cement.	Ordinary Portland Cement.	Iron-ore Cement.	Blastfurnace Cement.	Aluminous Cement.
$(NH_4)_2SO_4$	7	15	12	59	112
Na_2SO_4	63	97	227	Unattacked after 536 days	185
$MgSO_4$	97	210	77	362	Unattacked after 536 days
$CaSO_4$	500	Unattacked after 536 days.			
$MgCl_2$	} Unattacked after 536 days.				
Distilled water					

It will be seen that the resistance of the various cements to ammonium sulphate solution increases in the following order : high-strength Portland, iron-ore cement, ordinary Portland, blastfurnace and aluminous cement. Resistance to sodium sulphate solution increases in the following order : high-strength Portland, ordinary Portland, aluminous cement, iron-ore cement and blast-
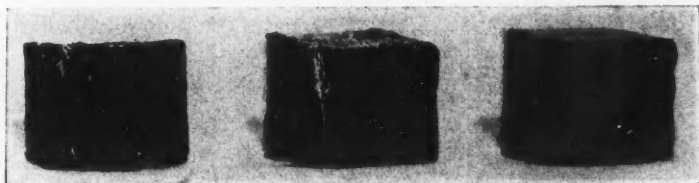

Fig. 45.—Cubes of ordinary Portland (left), high-strength Portland (centre), and aluminous cement (right) after 20 days in 15 per cent. ammonium sulphate solution.

furnace cement. Resistance to magnesium sulphate solution increases in the following order : high-strength Portland, iron-ore cement, ordinary Portland, blastfurnace and aluminous cement.

The progress of attack in the various solutions will first be described, after which the interpretation of the results will be discussed.

Ammonium Sulphate Solution.

HIGH-STRENGTH PORTLAND CEMENT.—After five days crystals are formed on the cubes, proved to be calcium sulphate. After seven days disintegration begins at the corners and edges. Fig. 45 (centre) shows the disintegration after
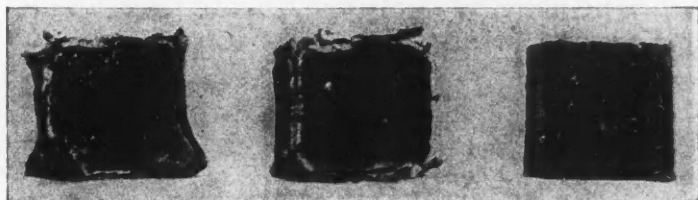
Fig. 46.—Cubes of ordinary Portland (left), high-strength Portland (centre), and aluminous cement (right) after 60 days in 15 per cent. ammonium sulphate solution.

20 days and Fig. 46 (centre) after 60 days. In 125 days the cube is entirely destroyed and covers the bottom of the storage vessel partly as a powder and partly in larger fragments.

ORDINARY PORTLAND CEMENT.—The first signs of decomposition appear on the edges and corners after 15 days. Attack then rapidly progresses, and Fig. 45 (left) shows the test-piece after 20 days. At 60 days the cube has prac-

tically the same appearance (Fig. 46, left) as the cube of high-strength Portland cement. In 125 days the cube of ordinary Portland has completely fallen to pieces.

ALUMINOUS CEMENT.—With this cement the commencement of attack is very delayed. After six weeks numerous gypsum crystals are formed on the surface of the cube (Fig. 46, right), and fine expansion cracks appear on the
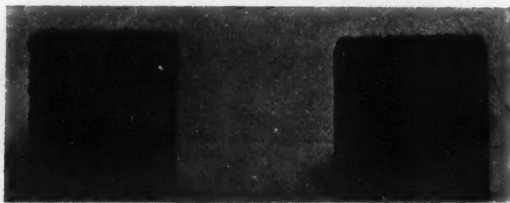

Fig. 47.—Cubes of iron-ore cement (left) and blastfurnace cement (right) after 20 days in 15 per cent. ammonium sulphate solution.

edges only after 112 days. Disintegration continues to proceed very slowly, so that after 536 days the cube presents the same appearance as the ordinary Portland cement cube at 20 days.

IRON-ORE CEMENT.—Iron-ore cement is attacked at practically the same rate as ordinary Portland. Disintegration at the corners and edges begins after 12 days and then proceeds very rapidly ; Fig. 47 (left) shows the result after 20 days. In 60 days the iron-ore and ordinary Portland cements are attacked to the same
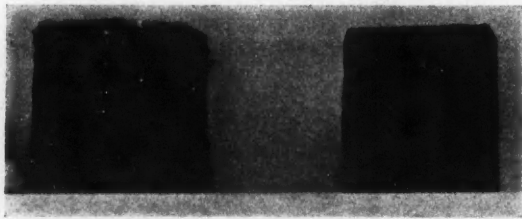
Fig. 48.—Cubes of iron-ore cement (left) and blastfurnace cement (right) after 60 days in 15 per cent. ammonium sulphate solution.

extent, as shown by a comparison of Fig. 48 (left) and Fig. 46 (left). After 90 days decomposition is very pronounced, and after 125 days the test-piece is completely destroyed.

BLASTFURNACE CEMENT.—In this case the attack first becomes evident after 59 days, in that one of the test-pieces shows a fine expansion crack. In 70 days both cubes have numerous cracks, which after 90 days have developed to the extent shown in Fig. 49. After a year the cubes are completely destroyed. The

disintegration is, however, different from that obtained with iron-ore and Port-land cements : the blastfurnace cement cube has split into larger lumps (Fig. 49), while the Portland and iron-ore cement cubes have fallen into a pasty mass.

The crystalline efflorescence formed on the test-pieces is chiefly calcium sulphate, as is clearly shown by Figs. 50 and 51.

Sodium Sulphate Solution.

HIGH-STRENGTH PORTLAND CEMENT.—The attack proceeds much more slowly than in ammonium sulphate solution, and the first expansion cracks are
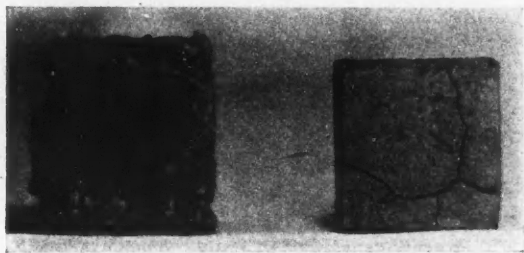
Fig. 49.—Cubes of iron-ore cement (left) and blastfurnace cement (right)
after 90 days in ammonium sulphate solution.

observed after 63 days. After about eighteen months (536 days) the cubes have the appearance shown in Fig. 52 (centre) : the corners and edges have swollen and the surface is softened.

Fig. 50.—Crystalline efflorescence of calcium sulphate on cement cubes stored in 15 per cent. ammonium sulphate solution.
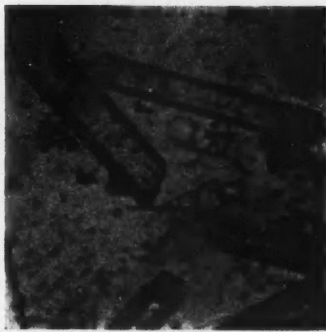
Fig. 51.—Calcium sulphate crystals from cement cubes stored in ammonium sulphate solution.

ORDINARY PORTLAND CEMENT.—Cubes of ordinary Portland cement are somewhat more resistant, and the first signs of attack are observed after 97 days. The appearance of the cubes after 536 days is shown in Fig. 52 (left).

ALUMINOUS CEMENT.—Aluminous cement is less resistant to sodium sulphate than to other sulphate solutions.   After 185 days fine cracks and scaling of the surface appear.   After 536 days the corners and edges are swollen and the surface can readily be scaled off (Fig. 52, right).   Below the scaled surface the cement is still unattacked.

IRON-ORE CEMENT.—Iron-ore cement is much more resistant to sodium sulphate solution than the Portland cements.   The first expansion cracks are found along certain edges after 227 days.   After 536 days the expansion phenomena have
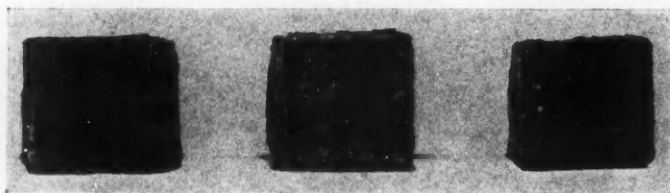

Fig. 52.—Cubes of ordinary Portland (left), high-strength Portland (centre), and aluminous cement (right) after 536 days in 15 per cent. sodium sulphate solution.

proceeded to such an extent that the appearance of the cubes (Fig. 53, left) is approximately the same as that of the Portland cement cubes (Fig. 52, left). Blastfurnace cement (Fig. 53, right) shows no sign of attack after 536 days.

Magnesium Sulphate Solution.

HIGH-STRENGTH PORTLAND CEMENT.—With this cement expansion cracks appear after 98 days and rapidly increase.   In one year the corners and edges are completely decomposed and the deterioration has proceeded much further
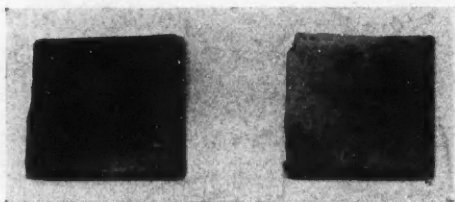

Fig. 53.—Cubes of iron-ore cement (left) and blastfurnace cement (right) after 536 days in 15 per cent. sodium sulphate solution.

than in the case of sodium sulphate solution.   Fig. 54 (centre) shows the cube after 536 days, and this may be compared with the cube stored in sodium sulphate (Fig. 52).

ORDINARY PORTLAND CEMENT.—This behaves very differently from high-strength Portland cement, and in this case visible signs of attack do not appear

until after 210 days. Attack proceeds more rapidly than in sodium sulphate solution.   The appearance of the cube after 536 days is shown in Fig. 54 (left).

ALUMINOUS CEMENT.—In contrast to the Portland cements, aluminous cement is absolutely unattacked even after 536 days. An efflorescence is formed on the surface of the cubes, which is found to consist of magnesium hydroxide.
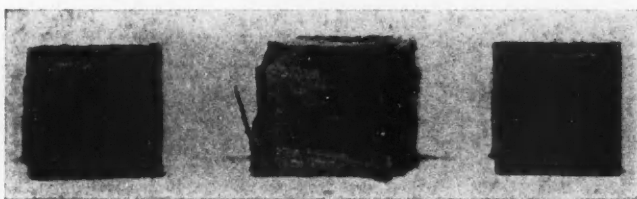

Fig. 54.—Cubes of ordinary Portland (left), high-strength Portland (centre), and aluminous cement (right) after 536 days in 15 per cent. magnesium sulphate solution.

IRON-ORE CEMENT.—Long fine cracks appear along the edges of the cubes after 77 days, and rapidly become wider.   Decomposition proceeds much more rapidly than in sodium sulphate solution.   At the end of one year the corners and edges are entirely broken away and the disintegration is similar to that found in the case of high-strength Portland cement.   Fig. 55 (left) shows the appearance of the cube after 536 days.
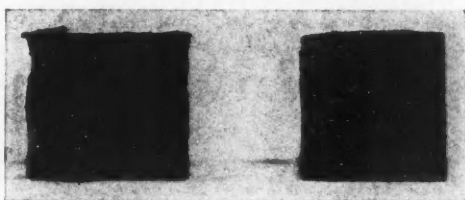

Fig. 55.—Cubes of iron-ore cement (left) and blastfurnace cement (right) after 536 days in 15 per cent. magnesium sulphate solution.

BLASTFURNACE CEMENT.—This is much more resistant than the Portland cements.   Only after the lapse of 362 days can fine cracks be observed along the edges, and decomposition proceeds extremely slowly.   The appearance of the cube after 536 days is shown in Fig. 55 (right).

Magnesium Chloride Solution.

The effects of this solution are shown in Figs. 56 and 57.   Even after 30 days the high-strength Portland cube is covered with a thick layer of magnesium hydroxide, which after 536 days has the appearance shown in Fig. 56 (centre). With ordinary Portland cement this white cheese-like efflorescence first appears

in 50 days and its further development is much slower (Fig. 56, left, at 536 days). The relatively slight resistance of iron-ore cement to magnesium salt solutions (*cf.* MgSO$_4$, Fig. 55, left) finds expression in the formation of a thick white layer of hydroxide even after ten days. On removal of this covering the surface of the cement is found to contain cracks and hollows. The appearance of the cube after 536 days is shown in Fig. 57 (left). Aluminous cement (Fig. 56, right)
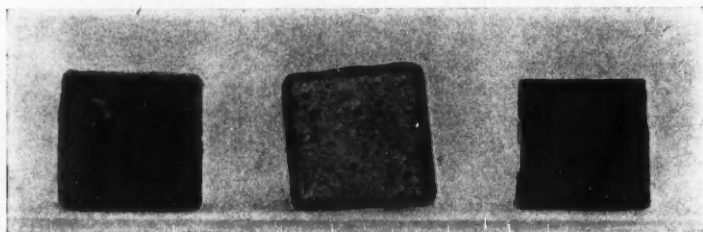

Fig. 56.—Cubes of ordinary Portland (left), high-strength Portland (centre), and aluminous cement (right) after 536 days in 15 per cent. magnesium chloride solution.

and blastfurnace cement (Fig. 57, right) show no signs of attack. The blast-furnace cement cubes are covered with an extremely thin uniform layer of magnesium hydroxide.

These experiments, in which the influence of such factors as particle size and temperature is eliminated, provide a reliable criterion of the cements investigated. They show that the resistance of the various cements to aggressive salt
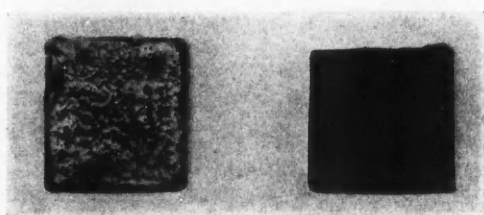

Fig. 57.—Cubes of iron-ore cement (left) and blastfurnace cement (right) after 536 days in magnesium chloride solution.

solutions increases in the order : (1) high-strength Portland cement, (2) ordinary Portland cement, (3) blastfurnace cement, (4) aluminous cement. Iron-ore cement behaves differently in different solutions. In sodium sulphate its resistance is greater than that of ordinary Portland cement, so that it falls between the latter and blastfurnace cement. In both magnesium salt solutions the resistance of iron-ore cement is less than that of ordinary Portland, so that its position in the series is between high-strength and ordinary Portland. The

inferiority of this particular iron-ore cement in magnesium salt solutions is presumably due to its relatively high lime content.   The Kühl lime saturation factor of this cement is higher than that of the Portland cement.   With the same lime saturation factor the iron-ore cement should offer the same resistance to magnesium solutions as ordinary Portland.

In sodium sulphate solution aluminous cement is less resistant than blast-furnace cement ; in all the other salt solutions investigated the aluminous cement is the most resistant.

The different resistance of the various cements to the attack of salt solutions will now be discussed. It has already been shown that the hydration, i.e., the setting and hardening, of cements proceeds by the removal of CaO from the calcium silicates with the formation of calcium hydrosilicates of lower lime content.   The attack of salt solutions is due to the penetration of the ions of

Fig. 58.—The hair-fine crystals are calcium sulpho-aluminate, the thick crystals calcium sulphate.

salt into the fine pores of the cement until they come into contact with the free $Ca(OH)_2$ formed by hydration.   The $Ca(OH)_2$ then reacts with these ions to form salts in accordance with the following equations :
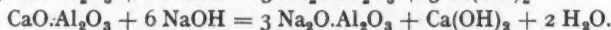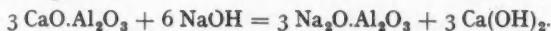
(1) $Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O.$

(2) $Ca(OH)_2 + (NH_4)_2SO_4 = CaSO_4 + 2NH_4OH.$

(3) $Ca(OH)_2 + Na_2SO_4 = CaSO_4 + 2NaOH.$

(4) $Ca(OH)_2 + MgSO_4 = CaSO_4 + Mg(OH)_2.$

(5) $Ca(OH)_2 + MgCl_2 = CaCl_2 + Mg(OH)_2.$

It is thus evident that the presence of SO_4-ions in the liquid surrounding a cement is always bound up with the formation of $CaSO_4$.   This is dissolved from the cement by the liquid and the ultimate destruction of the cement is thereby brought about.   The author's earlier work[25] has shown that all the phenomena observed in the solution and on the cement test-piece can be interpreted by these equations.   Shortly after immersing cement test-pieces in

[25] Probst and Dorsch, *Zement*, Nos. 10 and 11, 1929.

ammonium sulphate solution ammonia is formed, the smell of which is readily detected. This removal of ammonia is the reason for the extremely vigorous attack of ammonium sulphate solution. Similarly in the case of magnesium solutions $Mg(OH)_2$ is removed from solution as a white deposit which is found as a white efflorescence on the cement (Figs. 54 to 57).

The action of sodium sulphate solution on cement produces sodium hydroxide and calcium sulphate, and the formation of this hydroxide explains the different behaviour of the various cements in sodium sulphate. Iron-ore cement was found to be more resistant than Portland to this solution, while aluminous cement was much less resistant to sodium than to other sulphates. These differences are due to the different calcium aluminate contents of the cements and to the action of the NaOH formed on these aluminates. In Portland cement the Al_2O_3 content is 6 to 7 per cent. ; in iron-ore cement it is only 1 to 2 per cent. The NaOH formed on storage in sodium sulphate solution attacks the calcium aluminates of Portland cement forming soluble sodium aluminate, which is easily decomposed by sulphates. This sodium aluminate formation may be represented by the equations

$$3\ CaO.Al_2O_3 + 6\ NaOH = 3\ Na_2O.Al_2O_3 + 3\ Ca(OH)_2.$$
$$CaO.Al_2O_3 + 6\ NaOH = 3\ Na_2O.Al_2O_3 + Ca(OH)_2 + 2\ H_2O.$$

(The ternary zeolithic CaO-Al_2O_3-SiO_2 compounds of Portland and aluminous cements are similarly attacked. Exchange of lime results in the formation of sodium zeoliths of low strength and high solubility.) These reactions can only occur to a much less extent in iron-ore cement. With aluminous cement, however, they proceed as in Portland cement since aluminous cement consists chiefly of calcium aluminates.

Calcium sulphate in the form of large well-defined crystals has been observed in all the test-pieces examined by the author. Calcium sulpho-aluminate crystals, on the other hand, were very rarely observed, only a few isolated crystals of this double salt being found among many thousand calcium sulphate crystals. A particularly fine photomicrograph of the sulpho-aluminate was, however, obtained and is shown in Fig. 58.

The rare occurrence of the sulpho-aluminate is partially explained by recent work of Guttmann and Gille[26], according to which the concentrations of the salt solutions in scientific experiments are generally too high for its formation. My own experiments indicate that the decomposition of cement by calcium sulpho-aluminate is a secondary phenomenon. The primary cause of decomposition is the formation of $CaSO_4$ from $Ca(OH)_2$. The theory of the destructive effect of the sulpho-aluminate is contradicted by the facts that only gypsum crystals—and no sulpho-aluminate crystals—were found in aluminous cement, and that there was only slight deterioration due to the sulphates, although the high percentage of alumina presents the most favourable conditions for the formation of the sulpho-aluminate. To enable us to decide which of the two compounds is the chief cause of decomposition a cement of extremely low alumina content

[26] Guttman and Gille, *Tonind Zeit.*, p. 759, 1930.

may be used, for which sulpho-aluminate formation will be almost nil so that it cannot exert destructive action. For this purpose iron-ore cement was investigated, and, as already pointed out, was seriously attacked by sulphate solutions.

The corrosion of cement is thus seen to be dependent upon the presence of free $Ca(OH)_2$. The smaller the amount of $Ca(OH)_2$ set free during setting and hardening, the greater the resistance of the cement to the attack of salt solutions. The quantity of $Ca(OH)_2$ formed also determines the specific electrical conductivity. It was shown earlier that the conductivity decreases parallel with the resistance of the cement to chemical attack, in the order high-strength Portland cement, ordinary Portland cement, blastfurnace cement, and aluminous cement. Conductivity measurements on setting cement thus provide confirmation of the theory of decomposition described. The author's work presents the following points applicable to concrete practice. All cements differ in their resistance to chemical attack, and highly-resistant cement should be used where such attack is to be anticipated, i.e., in sea-water, rivers and lakes, and in certain
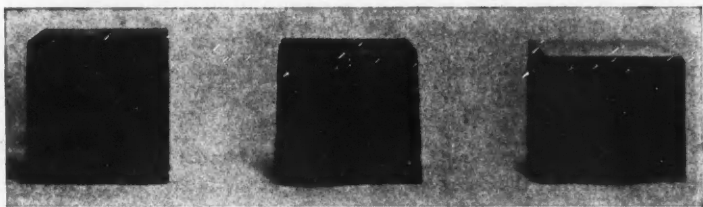

Fig. 59.—Cubes of ordinary Portland cement after 4 weeks in tap-water (left), distilled water (centre), and CO_2-water (right).

industrial installations. The cement chosen should in every case be that which offers the highest resistance to the particular type of solution in question. It should further be stated that the resistance to attack offered by different Portland cements, and also blastfurnace cements, varies greatly. For example, the resistance of Portland cement may be as great as that of many blastfurnace cements. The author has found that German Portland cements produced in various localities behave very differently in salt solutions, even though there is no great difference in the lime content. This indicates the great effect which the nature of the raw materials and the conditions of burning exert upon the resistance to chemical attack. This difference between cements from various localities also finds expression in the relation between crushing and tensile strengths and the water-cement factor. For example, the author found[27] that numerous north-German Portland cements were much less susceptible to change in the percentage of mixing water than Rhineland cements. It was also found that blastfurnace cements have only slight resistance to attack when produced from Portlands of low resistance.

[27] Dorsch, *Zement*, December, 1931.

Effect of Carbon Dioxide on Cement.

Carbon dioxide offers no exception to the rule that cements dissolve in acids, and decomposition of this kind is extremely common where water containing carbonic acid is in contact with concrete. This form of attack is again the subject of numerous publications, and again the value of the work is greatly lost because the materials and conditions are inadequately defined. The author therefore undertook a quantitative study of the action of carbon dioxide on cement. This investigation could not be carried out using natural waters for two reasons : first, the concentration and composition of such water continually change ; and, second, many natural waters contain hydrated ferric oxide which is deposited irregularly on the concrete and forms a protective layer. These objections were proved by tests in which cement test-pieces were stored in a CO_2-containing well water from the Black Forest. The cement was rapidly covered with a partially gelatinous coating of ferric hydroxide which prevented further access of the water. In addition analyses of samples of the water taken at different times gave very different results. It was therefore decided to study the attack of carbon dioxide on cement in the laboratory using pure materials.

For this purpose small cubes of pure Portland cement were prepared at 16 deg. C. using 28 per cent. mixing water. The percentage analysis of the cement was loss on ignition 1.35 ; insoluble residue 0.59 ; SiO_2, 20.24 ; CaO, 65.44 ; Al_2O_3, 5.82 ; Fe_2O_3, 3.61 ; MgO, 1.25 ; SO_3, 1.70.

The work was later extended to include blastfurnace and aluminous cements, and it was found that the deterioration of these cements due to CO_2 was approximately the same as that of Portland cement. After hardening one day in air and six days in water, two cubes each were stored in (1) tap-water, (2) distilled water, (3) water containing CO_2. In the last case CO_2 was continuously passed through the storage water so that it remained saturated. The three liquids were renewed weekly, and in each case the liquids removed were analysed. The test-pieces stored in the different liquids became very different in appearance.

(1) TAP-WATER.—The cement very slowly became coated with an extremely fine white layer, which analysis proved to be calcium carbonate. Fig. 59 (left) shows the test-piece after four weeks, and no further change was evident after 500 days.

(2) DISTILLED WATER.—Even after two weeks a layer of $CaCO_3$ was visible, which gradually increased in thickness. At four weeks there is an obvious difference between the cubes stored in tap-water and distilled water, the layer of $CaCO_3$ being much thicker in the latter case (Fig. 59, centre). After 500 days this layer is half a millimetre thick ; in places where it has become detached a second layer has already formed.

(3) CO_2-WATER.—In this case a white layer of $CaCO_3$ is evident even after two days, and in a week this has attained a thickness of $\frac{1}{4}$ mm. The coating then begins to break away and in four weeks is almost entirely detached (Fig. 59, right). In eight weeks it has disappeared and the cubes once more present a dark-coloured exterior. In 500 days the dark olive-green surface layer has

become softened and can be removed with a spatula to a depth of 2 mm. without difficulty.   Below this surface layer the cement is still hard.

TABLE IX.

Grammes of CaO in 100 c.c. water.

No. of Weeks.	Distilled Water.	CO_2-water.	Tap-water.
1	0.068	0.109	0.0910
2	0.032	0.167	0.0875
3	0.022	0.175	0.0825
4	0.020	0.180	0.0835
5	0.020	0.185	
6	0.019	0.190	
7	0.019	0.210	
8	0.018	0.215	
9	0.017	0.220	
10	0.017	0.232	
11	0.016	0.240	
12	0.016	0.250	
13	0.014	0.250	
14	0.013	0.260	
15	0.012	0.235	
16	0.012	0.222	
17	0.011	0.214	
18	0.010	0.200	
19	0.0095	0.197	
20	0.0095	0.184	
21	0.0090	0.180	
22	0.0080	0.175	
23	0.0080	0.170	
24	0.0070	0.165	
25	0.0060	0.160	
26	0.0060	0.155	
27	0.0050	0.160	
28	0.0045	0.160	
29	0.0045	0.152	
30	0.0040	0.160	
31	0.0040	0.163	
32	0.0035	0.147	
33	0.0035	0.135	
34	0.0035	0.168	
35	0.0030	0.184	
36	0.0030	0.152	
70	0.0020	0.148	0.0802

Table IX gives the chemical analyses of the three liquids removed from the test-pieces after storage.   It is seen that the amount of CaO dissolved in the tap-water remains almost constant (0.0835g. CaO per 100 c.c. water) from two weeks up to 500 days.   At the end of one week's storage the value is somewhat

higher (0.0910 g. CaO).   The value 0.0835 g. of CaO per 100 c.c. corresponds exactly to the lime content of the tap-water used, so that CaO is not dissolved from the cement, or at most only slightly.   A protective layer of $CaCO_3$ has been formed on the test-piece by the interaction of the CO_2 and CaO in the water, and this prevents solution of the CaO of the cement.

The analysis of the distilled water at the end of the first week gave 0.068 g. CaO per 100 c.c. water.   The CO_2 dissolved in the water rapidly forms a protective layer of $CaCO_3$ on the test-pieces and the amount of lime dissolved steadily diminishes until after 70 weeks only 0.002 g. CaO per 100 c.c. water is dissolved per week.

The amounts of lime dissolved are much higher in the case of the water through which CO_2 is passed.   A protective layer of $CaCO_3$ is formed in this case in the first week.   This is in turn partially redissolved by the action of the CO_2, and continuously reformed.   0.109 g. CaO per 100 c.c. is dissolved in the first week, and this amount continuously increases until in the fourteenth week 0.260 g. CaO per 100 c.c. is dissolved.. The protecting layer is by this time completely dissolved and the whole of the $Ca(OH)_2$ formed during setting is extracted to a depth of 1.5 mm.   At the end of 14 weeks the amount of dissolved CaO is reduced because of the lack of free CaO in the portion of the cement coming into contact with the liquid : after 70 weeks the dissolved CaO has fallen to 0.150 g. per 100 c.c.   The lime is now completely removed to a depth of 2 mm., and the colour of the test-piece is considerably deepened to dark olive-green owing to the increased proportion of Fe_2O_3 in the surface layer.

The surface layer of the test-pieces subjected to water containing CO_2 was analysed, after carefully scraping it off with a spatula.   The surface of the cement was found to be completely destroyed and could easily be removed to a depth of 2 mm.   Below this layer the cement was still strong and unattacked, while its colour was much lighter and identical with that at the beginning of the tests. The surface layer appears to exert a protecting influence, delaying the action of the CO_2, as is also indicated by the decreasing amounts of CaO dissolved. The soft surface material was dried, ignited, ground and analysed, with the following percentage results ; the values for the original cement are inserted in brackets : SiO_2, 50.84 (20.24) ; CaO, 16.14 (65.44) ; R_2O_3, 23.26 (9.43).   These figures clearly show that most of the CaO has been dissolved from the cement and that the SiO_2 and R_2O_3 have correspondingly increased.

The investigation shows that the decomposition of Portland cement in water containing CO_2 proceeds as follows.

(1) The CO_2 reacts at atmospheric pressure with the free lime of the cement, forming $CaCO_3$.

(2) The $CaCO_3$ so formed reacts with further CO_2 to form calcium bicarbonate, $Ca(HCO_3)_2$, according to the usual equation.

(3) The bicarbonate is either dissolved (enabling further attack on the cement by CO_2), or it reacts with free lime in the deeper layers of the cement according to the equation

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$
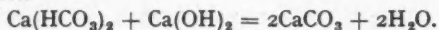
(4) The $CaCO_3$ so formed is again converted into the bicarbonate by reaction with further CO_2, and the bicarbonate reacts with free lime in still deeper layers of the cement.

Cement is thus progressively decomposed in successive stages by the action of water containing CO_2. The water comes into contact with a layer of high lime content and leaves behind after the reaction a layer of lower lime content. Ultimately the whole of the lime in the cement is dissolved out by the action of the CO_2. With this type of decomposition expansion does not occur, but in its place there is a gradual softening and decay of the cement, leading finally to complete disintegration.

(To be continued.)

Formation of Hydrates of CaSO₄ in Grinding Cement.

In a recent number of *Zement*, P. Schachtschabel states that gypsum heated over phosphorus pentoxide at 45 deg. C. can be dehydrated until it contains 0.76 per cent. water. On heating at 110 deg. for two months the residual water was 0.7 per cent. and at 165 deg., 0.3 per cent. In all these experiments X-ray analysis showed the presence of only the hemihydrate crystal lattice. The material obtained is that known as soluble anhydrite. It consists of partly dehydrated hemihydrate with water zeolithically held. (Hemihydrate contains 6.61 per cent. water.) Natural anhydrite or dead-burnt gypsum has an entirely different crystal lattice from hemihydrate. On heating soluble anhydrite below 200 deg. the change to natural anhydrite is very slow ; it is rapid only above 300 deg. Thus when gypsum is ground with cement it is partly converted to hemihydrate and at high mill temperatures to soluble anhydrite, and natural anhydrite is not formed. With a mill exit temperature of 90 deg. C. about half the gypsum, and at 120 deg. almost all the gypsum, may be so converted. The low setting time of high strength and other finely-ground cements is partly due to the presence of large amounts of hemihydrate and soluble anhydrite.

INTERNATIONAL DICTIONARY OF CEMENT.

Arranged by Dr. C. R. Platzmann, with collaborators in England, France, and Spain.

French.	English.	German.	Spanish.
		E	
eau	water	Wasser	agua
eau de gâchage	mixing water	Anmachewasser	agua de amasado
eau de mer	sea water	Seewasser	agua del mar
eau potable	tap water	Trinkwasser	agua ordinaria
échafaudage, ossature	gantry	Gangbrücke	conducto de protección
échange de chaleur	heat exchange	Wärmeaustausch	intercambio de calor
échantillon	specimen	Probe	probeta
effort de compression	compressive stress	Druckspannung	esfuerzo de compresión
effort de flexion	bending stress	Biegespannung	esfuerzo de flexión
électrode collectrice	collecting electrode	Abscheidungselektrode	electrodo captador
électrode émettrice	discharge electrode	Entladungs-, Abscheidungselektrode	electrodo de descarga
élingue	sling	Schlinge	cuerda
embarilleuse	barrel packing machine	Fasspackmaschine	envasadora
embrayage (appareil d')	clutch	Kupplung	embrague
embrayage magnétique	magnetic clutch	Magnetkupplung	embrague magnetico
énergie	power	Kraft	energía
énergie électrique	electric power	elektr. Kraft	energia eléctrica
enfermé	enclosed	gekapselt	cerrado
enfournement par pulvérisation	spray feed	Sprühaufgabe	alimentación por surtidores
engrenage conique	bevel drive	Kegelradantrieb	engranaje conico
engrenage droit ; roue d'engrenage	spur gear	Stirnradgetriebe	engranaje recto o cylindrico
engrenage réducteur	reduction gear	Reduziergetriebe	reductor de engranaje
entrefer	air gap	Luftspalt	entrehierro
entrepot	{store {warehouse	Vorratslager Lagerhaus	almacén almacén
entretien	maintenance	Unterhaltung, Wartung	funcionamiento
enveloppe du four	kiln shell	Ofenmantel	cubierta del horno
épreuve d'invariabilité de volume	soundness test	Raumbeständigkeitsprüfung	ensayo de inalterabilidad de volumen
épreuve d'ébullition	boiling test	Kochprobe	ensayo a la ebullición
épreuve sur galette comprimée et etuvée	compressed-pat kiln test	Presskuchendarrprobe	ensayo de galleta comprimida
éprouvette	test sample	Probekörper	probeta
éprouvette graduée	graduated measuring tube	graduiertes Messrohr	probeta graduada
équipement dépoussiéreur	dust-collecting plant	Staubsammlungsanlage	instalación de captación de polvo
essai	testing	Prüfung, Versuch	ensayo
essai à l'eau froide	cold water test	Kaltwasserprobe	ensayo al agua fria
essayer	test, to	prüfen, untersuchen	ensayar
éteindre (la chaux)	slake, to	löschen	apagar
évaporation	evaporation	Verdampfung, Verdunstung	evaporación
excavateur	excavator	Bagger	excavadora
excavateur à cables	dragline excavator	Bagger mit Leitseil, Schrapper	excavadora o draga de cable

French.	English.	German.	Spanish.
excavateur à vapeur	steam navvy	Dampfbagger	pala mecánica
excavateur, grue	excavating machine	Löffelbagger	máquina excavadora
excès	{ surplus	Ueberschuss	exceso
	{ excess	Ueberschuss	exceso
expansion	expansion	Treiben, das	expansión
expédition	dispatch	Verladung ; Verladen, das	despacho de mercancías
explosif	explosive	Sprengstoff	explosivo
extraction	extraction	Absacken, das Abziehen, das	extracción

F

fabrication de ciment	cement manufacture	Zementherstellung	fabricación del cemento
facteur de puissance	power factor	Leistungsfaktor	factor de potencia
faire le vide	exhaust, to	entleeren, ausschöpfm	agotar, extraer
farine, sablette	grit	Gries	material triturado
fendillement	{ crack	Riss	raja
	{ craze	Sprung	grieta
fendillement dû au retrait	crack due to contraction	Schwindriss	grieta debida a la contracción
fendillement sur le bord	edge crack	Kantenriss	grieta ó raja en el borde
fer	iron	Eisen	hierro
fer coulé	semi-steel	Flusstahl	semi-acero
fer puddlé ; fer battu	wrought iron	Schmiedeeisen	hierro forjado ; hierro batido
fil	wire	Draht	hilo, alambre
filtre à disque	disk filter	Scheibenfilter	filtro de discos
finesse de mouture	fineness	Mahlfeinheit	finura
fissure due à l'expansion	crack due to expansion	Treibriss	grieta debida a la dilatación
flèche	deflection	Durchbiegung	flecha
fondant	flux	Flussmittel	fundente
fonderie	foundry	Giesserei	fundición
fonte	cast iron	Gusseisen	fundición de hierro
fonte malléable	malleable iron	Tempergusseisen	hierro maleable
force centrifuge	centrifugal force	Zentrifugalkraft	fuerza centrífuga
fosse	pit	Grube	cantera
four	kiln	Ofen	horno
four à water-jacket	water jacketed furnace	Wassermantelofen	horno con camisa de agua
four circulaire	circular kiln	Ringofen	horno circular
four continu	continuous working kiln	Ofen mit ständigem Betrieb	horno de marcha continua
four rotatif	rotary kiln	Drehofen, Rotierofen	horno rotatorio
four vertical	shaft kiln	Schachtofen	horno vertical
four vertical à grille tournante	rotary grate shaft kiln	Drehrostschachtofen	horno vertical de parrilla rotatoria
fourneau à mouffle	muffle furnace	Muffelofen	horno de mufla
fragilité	brittleness	Brüchigkeit	fragilidad
fragments (tomber en)	crumble, to	zerbröckeln	desmenuzarse
frottement	friction	Reibung	rozamiento
fumée	fume	Rauch	humo
funiculaire aérien	ropeway	Seilbahn	transportador aéreo de cable
fusion	fusion	Schmelzen, das	fusión

G

gâcher	gauge, to	anmachen	amasar
garder	cure, to	lagern	conservar
garnissage du four	kiln lining	Ofenfutter	forro o revestemiento del horno
galet du four	roller for kiln	Ofenwalzlager	rodillos para los hornos
galette de ciment	pat of cement	Zementkuchen	galleta de cemento

FRENCH.	ENGLISH.	GERMAN.	SPANISH.
garnissage du four rotatif	rotary kiln lining	Drehofenfutter	revistimiento refractario del horno rotatorio
gaz brulé	exit gas	Abgas	gas de escape
gaz de fours à coke	coke oven gas	Koksofengas	gas del horno de coke
gel	gel	Gel	gel
godet	bucket	Becher	cangilón
gonfler	expand, to	treiben	hinchar
gorge	groove	Rille, Verengung, Kehle	garganta, acanaladura
goujon ; tourillon	gudgeon	Zapfen ; Bolzen	chareta
graduer, classer	calibrate, to	kalibrieren	calibrar
graisse	grease	Fett	grasa
grille	grate	Rost	parrilla
grille en acier fondu	cast steel grating	Gusstahlgreting	parrilla de acero fundido
grille mécanique	travelling grate	Wanderrost	parrilla transportadora
grosseur de grain	grain size	Korngrösse	grano mezclado
grossissement	magnification	Vergrösserung	aumento
grossiér	coarse	grob	grueso
grue	crane	Kran	grúa
grue à benne preneuse	grab-crane	Greiferkran	grúa de cuchara prensora
grue, excavateur	excavating machine	Löffelbagger	pala, maquina excavadora
gypse	gypsum	Gips	yeso

<div align="center">H</div>

haut fourneau	blast furnace	Hochofen	alto horno
herse, râble	harrow	Egge	castrillo
houille demi-grasse	gas coal	Gaskohle	carbón semi-graso
huile	oil	Oel	aceite
humidité	{humidity	Feuchtigkeit	humedad
	{moisture	Feuchtigkeit	humedad
humidité de l'air	air moisture	Luftfeuchtigkeit	humedad del aire
hydrate de chaux	{calcium hydroxide	Kalkhydrat	hidrato de cal
	{hydrate of lime	Kalkhydrat	hidrato de cal
hydrogène	hydrogen	Wasserstoff	hidrógeno

<div align="center">I</div>

impénétrable à la poussière	dustproof (dust-tight)	staubfrei (staubdicht)	herméticamente cerrado al polvo
imperméabilité	impermeability	Undurchlässigkeit	impermeabilidad
incuit	insufficiently burnt	Schwachbrand	cocción insuficiente
incuits	underburnt material	Leichtbrand	material mal cocido
installation de force motrice	power plant	Kraftanlage	centrale de fuerza
interrupteur	switchgear	Schaltgetriebe	interruptor
interrupteur à mercure	mercury switch	Quecksilberschalter	interruptor de mercurio
invariabilité, stabilité de volume	soundness	Raumbeständigkeit	estabilidad de volumen ; constancia de volumen
isolateur	insulator	Isolator	aislador

<div align="center">J</div>

jante à denture droite	spur rim	Zahnkranz	corona dentada
jeu	clearance	Toleranz	huelgo
joint	joint	Gelenk, Fuge	junta
joint élastique	flexible coupling	Gelenkkupplung	acoplamiento elástico
journal, revue, coussinet	journal	Zeitschrift, Lager	revista

<div align="center">(To be continued.)</div>